Hydride Reduction of $[(\eta^5\text{-Indenyl})Fe(CO)_3]BF_4$: Evidence for $(\eta^5\text{-Indenyl})(CO)_2FeCHO$ and $(\eta^5\text{-Indenyl})(CO)_2FeH$

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Although the hydride $(\eta^5\text{-Cp}(CO)_2FeH$ is well documented (see ref. 1 and refs. therein) and the corresponding formyl $(\eta^5\text{-Cp})(CO)_2FeCHO$ more recently identified by low temperature ^{1}H NMR spectroscopy [2], there have been, to the best of our knowledge, no previous reports of the analogous indenyl compounds. We report now spectroscopic (IR and ^{1}H NMR) evidence for these compounds by reduction of the tricarbonylindenyliron cation $[(\eta^5\text{-In})Fe(CO)_3]^+$ (**1**) by sodium borohydride in acetone.

Experimental

Typically for the low temperature IR studies, cation **1** (0.06 g) was dissolved in acetone (20 ml) at −80 °C and $NaBH_4$ (0.007 g), also in acetone (5 ml), was added at −80 °C. After stirring briefly (*c.* 2 min), a sample was withdrawn for immediate IR analysis in the region 1700–2200 cm^{-1}, using low-temperature cells. Monitoring by low-temperature ^{1}H NMR was performed as follows: to a solution of cation **1** in acetone-d$_6$ (15 mg in 0.6 ml) in an NMR tube at −80 °C was added a solution of $NaBH_4$ in acetone-d$_6$ (2 mg in 0.4 ml) at −80 °C, with both solutions under argon. A solution of **3** was prepared by the same method [1] as the analogous $(\eta^5\text{-Cp})(CO)_2FeH$, namely, by treating 20 ml of a solution of the dicarbonylindenyliron anion, $[(\eta^5\text{-In})Fe(CO)_2]^-$, with glacial acetic acid (5 ml) at 0 °C under nitrogen. $[(\eta^5\text{-In})Fe(CO)_2]^-$ was prepared by reducing $[(\eta^5\text{-In})Fe(CO)_2]_2$ (**4**) (1.00 g) with sodium amalgam (1.00 g of sodium in 100 ml of mercury in THF (70 ml), stirring for 1 h under nitrogen and subsequent removal of the amalgam by separation). A sample of **3** was also prepared for NMR studies but on a reduced scale (50 mg of **4** in 5 ml THF-d$_8$) under argon and at 0 °C. Attempts to isolate **3** resulted only in decomposition and reformation of the dimer **4**. NMR spectra were measured on a JEOL GX 270 MHz instrument. IR spectra were obtained on a Perkin-Elmer 1720 FT-IR spectrometer linked to a 3700 data station.

Results and Discussion

The initial IR spectrum of the cation **1** treated with $NaBH_4$ in acetone at −80 °C, as described above, showed peaks at 2040 and 1992 cm^{-1}, with virtually no absorption from cation **1** (ν(CO) = 2117 and 2069 cm^{-1}). On warming to −10 °C, the above peaks were replaced by ν(CO) = 2011 and 1950 cm^{-1}. A solution of **3** prepared directly from the dicarbonylindenyl anion as above also showed peaks at 2011 and 1950 cm^{-1}. Thus, the peaks observed at −10 °C in the reaction of **1** with borohydride in acetone are assigned to the hydride **3** and those at −60 °C (2040 and 1992 cm^{-1}) to the formyl **2**, since at this temperature the ^{1}H NMR spectrum gives

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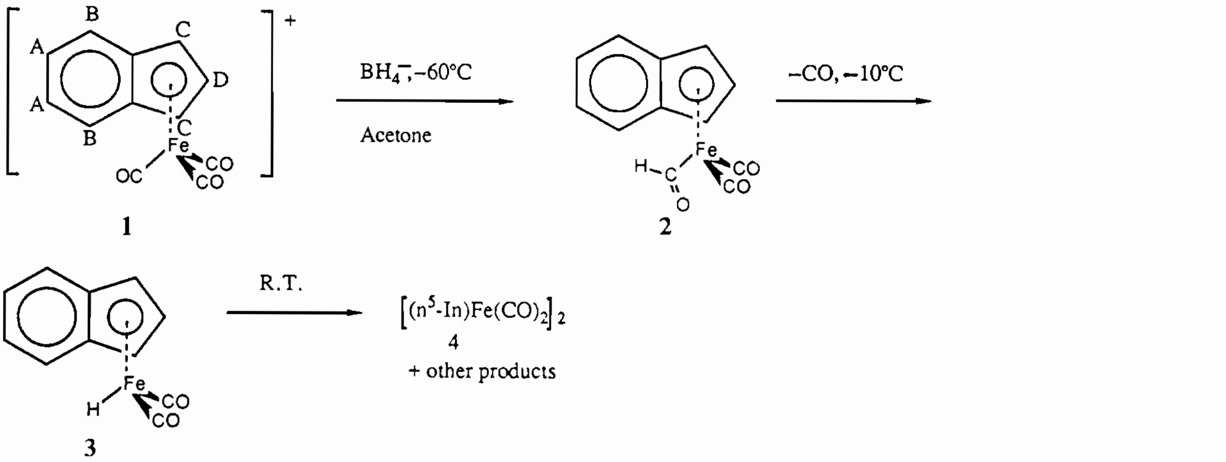

clear evidence for a metal-formyl (see below). The IR study was repeated in acetone-d_6 for direct comparison with the NMR study and very similar frequencies were obtained (at -60 °C ν(CO) = 2039 and 1992 cm^{-1}; at -10 °C ν(CO) = 2010 and 1951 cm^{-1}). To the solution of cation **1** in acetone-d_6 was added $NaBH_4$, as described above. At -80 °C, resonances developed at δ 12.79 ppm characteristic of a metal-formyl hydrogen [3], together with peaks in the region of δ 7.5 ppm due to an A_2B_2 system of the six-membered ring, and at δ 6.30 (d, J_{CD} 2.79 Hz, C, 2H) and δ 5.45 (t, J_{CD} 2.79 Hz, D, 1H) due to the three hydrogens of the five-membered ring of the iron formyl **2**. Resonances due to cation **1** were also present in the δ 7.9 region and were assigned to the A_2B_2 system, and at δ 6.68 (d, J_{CD}, 2.75 Hz, C, 2H) and δ 6.35 ppm (t, J_{CD} 2.75 Hz, D, 1H). As the temperature was raised to -50 °C, the peaks of the formyl **2** were replaced by a new resonance at δ -15.34 (upfield from TMS $\delta = 0$), characteristic of a metal-hydride hydrogen, and ring resonances in the δ 7.5 ppm region were assigned to the A_2B_2 system of the six-membered ring, and δ 5.54 (d, J_{CD} 2.94 Hz, C, 2H) and δ 5.63 (t, J_{CD} 2.94 Hz, D, 1H) to the three hydrogens of the five-membered ring of the metal hydride **3**. As in the IR studies, a sample of **3** was prepared from the indenyl dimer **4** in THF-d_8, as described above. The ^1H NMR spectra showed resonances at δ -15.37 ppm and ring hydrogen resonances for the A_2B_2 system in the region δ 7.25 and at δ 5.12 (d, C, 2H) and δ 5.21 (t, D, 1H). These latter peaks for the hydride **3** are inverted with respect to the formyl **2** but their assignments were confirmed by decoupling experiments and integrations.

The NMR results confirm the IR studies and show that reduction of cation **1** by sodium borohydride in acetone at -80 °C results in initial hydride attack on a metal-carbonyl group to form $(\eta^5\text{-In})(CO)_2FeCHO$ (**2**) which is only stable below about -55 °C. On raising the temperature to -50 °C, the formyl is replaced by the hydride $(\eta^5\text{-In})(CO)_2FeH$ (**3**) which remains stable in solution up to about 0 °C. The identity of **3** follows from a comparison of the IR and ^1H NMR spectra of the reaction mixtures at -10 °C with those of the independently synthesized hydride solutions. All attempts to isolate **2** and **3** were unsuccessful.

Raising the temperature of either the reaction mixture or hydride solutions to 25 °C gave the indenyl dimer **4** but the ^1H NMR spectra become very complex, probably due to the formation of a number of ring hydride-addition compounds as well as the dimer, which contrasts with the analogous Cp series where only the dimer is fomed [2]. Further studies of these reactions are in progress.

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